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(54) Title: AMINOPLAST-CURABLE FILM-FORMING COMPOSITIONS PROVIDING FILMS HAVING RESISTANCE TO ACID ETCHING (57) Abstract An aminoplast-curable film-forming composition is disclosed. The film-forming composition is a crosslinkable composition comprising (1) a material containing a plurality of carbamate and/or urea functional groups and (2) an aminoplast crosslinking agent. The composition provides a coating with improved acid etch resistance, making the coating particularly useful as an automotive clear coat.		

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AMINOPLAST CURABLE FILM-FORMING COMPOSITIONS
PROVIDING FILMS HAVING RESISTANCE TO ACID ETCHING

5

Field of the Invention

The present invention relates to aminoplast curable film-forming compositions, and in particular to aminoplast curable compositions exhibiting superior acid etch resistance.

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Background of the Invention

Aminoplast-cured coating systems are well known and provide many excellent coating properties. However, it is widely recognized that such coatings, particularly clear coats, have poor resistance to etching by acid. Conventional coating systems that contain hydroxyl functional film-forming resins and aminoplast crosslinking agents rely on a cure mechanism wherein hydroxyl groups on the resin react with the aminoplast to form ether linkages. See, for example, European Patent Application 0 257 848. Although not intending to be bound by any theory, it is believed that such ether linkages are vulnerable to acid attack and hence yield coatings with poor acid etch resistance.

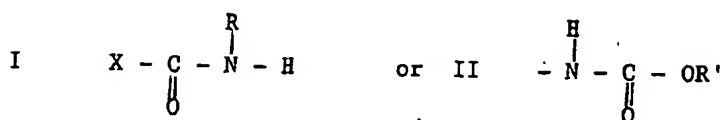
Because many geographic areas encounter acidic precipitation, acid resistance in coatings is becoming an increasingly desirable property, particularly for automotive coatings. Hydroxyl-aminoplast coating systems of the prior art are not highly effective for providing protection against etching caused by acid rain.

It is desirable, therefore, to provide a coating system which avoids the problems of the prior art by demonstrating improved acid etch resistance properties.

Summary of the Invention

In accordance with the present invention, a curable film-forming composition is provided, derived from (1) a material containing a plurality of terminal or pendant groups of the structure:

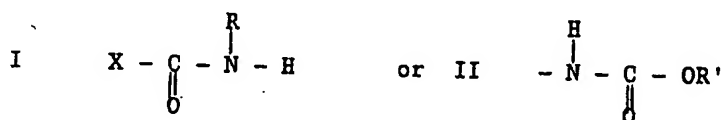
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where X is -N or -O and R is H or alkyl of 1 to 18 carbon atoms or R is bonded to X and forms part of a 5 or 6 membered ring and R' is alkyl of 1 to 18 carbon atoms; and (2) an aminoplast crosslinking agent containing methylol and/or methylol ether groups. Prior to crosslinking, the film-forming composition comprising the material of (1) and (2) has a calculated hydroxyl value less than 50 based on solid weight of the clear film-forming composition, excluding any hydroxyl functionality which may be associated with N-methylol groups. The crosslinked coating has a substantial number of urethane and/or urea crosslinks that arise from reaction of the terminal or pendant groups of structure I or II with the aminoplast, thereby providing a high level of acid etch resistance.

Detailed Description

The film-forming composition is a crosslinkable composition comprising (1) a material containing a plurality of pendant or terminal groups of the structure:



where X is -N or -O and R is H or alkyl of 1 to 18, preferably 1 to 6 carbon atoms or R is bonded to X and forms part of a five- or six-membered ring and R' is alkyl of 1 to 18, preferably 1 to 6 carbon atoms; and (2) an aminoplast crosslinking agent containing methylol and/or methylol ether groups. The material of (1) has on average at least two pendant or terminal groups of the structure I and/or II, preferably structure I, per molecule. Preferably X = -O. The material of (1) may be an acrylic polymer, a polyester polymer or oligomer, a polyurethane polymer or oligomer, or a blend of two or more of these materials. Acrylic polymers are preferred. Prior to crosslinking, the film-forming composition of (1) and (2) has a theoretical hydroxyl value of less than 50, preferably less than 25, and more preferably 0, based on solid weight of the film-forming

composition, excluding any hydroxyl functionality associated with N-methylol groups such as those in the aminoplast and any hydroxyl functionality which may be associated with N-methylol groups incorporated into the material of (1) such as N-methylol acrylamide groups in the acrylic polymer. By calculated hydroxyl value is meant the calculated value based on the relative amounts of the various ingredients used in making the film-forming composition, rather than the actual hydroxyl value which is measured on the film-forming composition itself by conventional techniques. The resultant crosslinked coating contains a substantial number of urethane or urea crosslinks that arise from reaction of the terminal or pendant groups of structure I or II with the aminoplast, thereby providing a high level of acid etch resistance.

The acrylic materials are copolymers of one or more alkyl esters of acrylic acid or methacrylic acid, and, optionally, one or more other polymerizable ethylenically unsaturated monomers. Suitable alkyl esters of acrylic or methacrylic acid include methyl methacrylate, ethyl methacrylate, butyl methacrylate, ethyl acrylate, butyl acrylate, and 2-ethylhexyl acrylate. Suitable other polymerizable ethylenically unsaturated monomers include vinyl aromatic compounds such as styrene and vinyl toluene; nitriles such as acrylonitrile and methacrylonitrile; vinyl and vinylidene halides such as vinyl chloride and vinylidene fluoride and vinyl esters such as vinyl acetate; and acid functional monomers such as acrylic and methacrylic acid.

Hydroxyl functional monomers such as hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, and hydroxypropyl methacrylate may be copolymerized with the acrylic monomers to impart hydroxyl functionality to the acrylic material in accordance with the theoretical hydroxyl values mentioned above.

Pendant carbamate functional groups of structure I ($X = -O$) may be incorporated into the acrylic polymer by copolymerizing the acrylic monomers with a carbamate functional vinyl monomer, for example a carbamate functional alkyl ester of methacrylic acid. These carbamate functional alkyl esters are prepared by reacting, for example, a hydroxyalkyl carbamate, such as the reaction product of

ammonia and ethylene carbonate or propylene carbonate, with methacrylic anhydride. Other carbamate functional vinyl monomers are, for instance, the reaction product of hydroxyethyl methacrylate, isophorone diisocyanate, and hydroxypropyl carbamate (yielding structure I), or the reaction product of hydroxypropyl methacrylate, isophorone diisocyanate, and methanol (yielding structure II). Still other carbamate functional vinyl monomers may be used, such as the reaction product of isocyanic acid (HNCO) with a hydroxyl functional acrylic or methacrylic monomer such as hydroxyethyl acrylate, and those described in U.S. Patent 3,479,328. Pendant carbamate groups can also be incorporated into the acrylic polymer by reacting a hydroxyl functional acrylic polymer with a low molecular weight alkyl carbamate such as methyl carbamate. Reference is made to Japanese Kokai 51-4124. Also, hydroxyl functional acrylic polymers can be reacted with isocyanic acid yielding pendant carbamate groups. Note that the production of isocyanic acid is disclosed in U.S. Patent 4,364,913. Likewise, hydroxyl functional acrylic polymers can be reacted with urea to give an acrylic polymer with pendant carbamate groups.

Pendant urea groups of structure I ($X = -N$) may be incorporated into the acrylic polymer by copolymerizing the acrylic monomers with urea functional vinyl monomers such as urea functional alkyl esters of acrylic acid or methacrylic acid. Examples include the condensation product of acrylic acid or methacrylic acid with a hydroxyalkyl ethylene urea such as hydroxyethyl ethylene urea. Other urea functional monomers are, for example, the reaction product of hydroxyethyl methacrylate, isophorone diisocyanate, and hydroxyethyl ethylene urea.

Mixed pendant carbamate and urea groups may also be used.

The acrylic polymer material may be prepared by solution polymerization techniques in the presence of suitable catalysts such as organic peroxides or azo compounds, for example, benzoyl peroxide or N,N -azobis(isobutyronitrile). The polymerization may be carried out in an organic solution in which the monomers are soluble by techniques conventional in the art. Alternately, the acrylic polymer may be prepared by aqueous emulsion or dispersion polymerization techniques well known in the art.

The acrylic material typically has a number average molecular weight of from about 900 to 13,000, preferably from about 1000 to 5000 as determined by gel permeation chromatography using a polystyrene standard, and an equivalent weight of less than 5000, preferably within the range of 140 to 2500, based on equivalents of reactive pendant or terminal carbamate or carbamate and/or urea groups. The equivalent weight is a calculated value based on the relative amounts of the various ingredients used in making the acrylic material and is based on solids of the acrylic material.

10 Polyesters may also be used in the formulation of the film-forming composition and may be prepared by the polyesterification of a polycarboxylic acid or anhydride thereof with polyols and/or an epoxide. Usually, the polycarboxylic acids and polyols are aliphatic or aromatic dibasic acids and diols.

15 The polyols which are usually employed in making the polyester include alkylene glycols, such as ethylene glycol, 1,6-hexanediol, neopentyl glycol, 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate and other glycols, such as hydrogenated Bisphenol A, cyclohexanediol, cyclohexanedimethanol, 20 caprolactone-based diols, for example, the reaction product of epsilon-caprolactone and ethylene glycol, hydroxy-alkylated bisphenols, polyether glycols, for example, poly(oxytetramethylene) glycol and the like. Polyols of higher functionality may also be used. Examples include trimethylolpropane, trimethylolethane, 25 pentaerythritol and the like.

The acid component of the polyester consists primarily of monomeric carboxylic acids or anhydrides thereof having 2 to 18 carbon atoms per molecule. Among the acids which are useful are phthalic acid, isophthalic acid, terephthalic acid, 30 tetrahydrophthalic acid, hexahydrophthalic acid, methyl hexahydrophthalic anhydride, adipic acid, azelaic acid, sebacic acid, maleic acid, glutaric acid, decanoic diacid, dodecanoic diacid and other dicarboxylic acids of various types. The polyester may include minor amounts of monobasic acids such as benzoic acid, stearic acid, 35 acetic acid, and oleic acid. Also, there may be employed higher carboxylic acids such as trimellitic acid and tricarballic acid.

Where acids are referred to above, it is understood that anhydrides thereof which exist may be used in place of the acid. Also, lower alkyl esters of the acids such as dimethyl glutarate and dimethyl terephthalate may be used.

5 Pendant carbamate functional groups of structure I may be incorporated into the polyester by first forming a hydroxyalkyl carbamate which can be reacted with the polyacids and polyols used in forming the polyester. A polyester oligomer may be prepared by reacting a polycarboxylic acid such as those mentioned above with a
10 hydroxyalkyl carbamate. An example of a hydroxyalkyl carbamate is the reaction product of ammonia and ethylene carbonate or propylene carbonate. The hydroxyalkyl carbamate is condensed with acid functionality on the polyester or polycarboxylic acid, yielding pendant carbamate functionality. Pendant carbamate functional groups
15 of structure I may also be incorporated into the polyester by reacting isocyanic acid or a low molecular weight alkyl carbamate such as methyl carbamate with a hydroxyl functional polyester. Also, pendant carbamate functionality may be incorporated into the polyester by reacting a hydroxy functional polyester with urea.

20 Pendant urea groups of structure I may be incorporated into the polyester by reacting a hydroxyl functional urea such as a hydroxyalkyl ethylene urea with the polyacids and polyols used in making the polyester. A polyester oligomer can be prepared by reacting a polyacid with a hydroxyl functional urea. Also,
25 isocyanate terminated polyurethane or polyester prepolymers may be reacted with primary amines, aminoalkyl ethylene urea, or hydroxyalkyl ethylene urea to yield materials with pendant urea groups. Preparation of these polymers is known in the art and is described in U.S. Patent No. 3,563,957.

30 Mixed pendant carbamate and urea groups may also be used in the polyester material.

Polyurethanes can be formed by reacting a polyisocyanate with a polyester having hydroxyl functionality and containing the pendant carbamate and/or urea groups. Alternatively, the polyurethane
35 can be prepared by reacting a polyisocyanate with a polyester polyol and a hydroxyalkyl carbamate or isocyanic acid as separate

reactants. Examples of suitable polyisocyanates are aromatic and aliphatic polyisocyanates, with aliphatic being preferred because of better color and durability properties. Examples of suitable aromatic diisocyanates are 4,4'-diphenylmethane diisocyanate, 5 1,3-phenylene diisocyanate, 1,4-phenylene diisocyanate, and toluene diisocyanate. Examples of suitable aliphatic diisocyanates are straight chain aliphatic diisocyanates such as 1,4-tetramethylene diisocyanate and 1,6-hexamethylene diisocyanate. Also, cycloaliphatic diisocyanates can be employed and are preferred 10 because of imparting hardness to the product. Examples include 1,4-cyclohexyl diisocyanate, isophorone diisocyanate, alpha,alpha-xylylene diisocyanate and 4,4'-methylene-bis-(cyclohexyl isocyanate).

The polyester or polyurethane materials typically have 15 number average molecular weights of about 300 to 3000, preferably about 300 to 600 in solvent borne systems and about 900 to 1500 in water borne systems as determined by gel permeation chromatography using a polystyrene standard, and an equivalent weight of from about 140 to 2500 based on equivalents of pendant carbamate and/or urea 20 groups. The equivalent weight is a calculated value based on the relative amounts of the various ingredients used in making the polyester or polyurethane and is based on solids of the material.

Besides polymeric materials, relatively low molecular weight materials containing pendant carbamate functional groups of structure 25 II may be formed by reacting isocyanate terminated monomers or oligomers, such as an isocyanurate of polymeric 1,6-hexamethylene diisocyanate, with an alcohol. Any suitable aliphatic, cycloaliphatic, aromatic alkyl monoalcohol or phenolic compound may be used, such as, for example, aliphatic alcohols containing from 1 30 to 18, preferably lower aliphatic alcohols containing from 1 to 6 carbon atoms such as methanol, ethanol, n-butyl alcohol and n-hexanol; cycloaliphatic alcohols such as cyclohexanol; aromatic-alkyl alcohols such as phenyl carbinol and methylphenyl carbinol; phenolic compounds such as phenol itself, and substituted 35 phenols in which the substituents do not adversely affect coating operations. Examples include cresol and nitrophenol.

It is possible to prepare blends of the acrylic, polyester, and polyurethane materials containing pendant or terminal carbamate and/or urea groups described above. It is also possible to prepare blends of the low molecular weight materials containing pendant carbamate and/or urea groups with the polymeric materials containing pendant carbamate and/or urea groups. The weight ratio of low molecular weight materials to polymeric materials may range from 10:90 to 90:10, preferably 10:90 to 40:60.

The film-forming composition also includes an aminoplast crosslinking agent containing methylol and/or methylol ether groups. Aminoplast condensates are obtained from the reaction of formaldehyde with an amine or amide. The most common amines or amides are melamine, urea, or benzoguanamine, and are preferred. However, condensates with other amines or amides can be used; for example, aldehyde condensates of glycoluril, which give a high melting crystalline product which is useful in powder coatings. While the aldehyde used is most often formaldehyde, other aldehydes such as acetaldehyde, crotonaldehyde, and benzaldehyde may be used.

The aminoplast contains methylol groups and preferably at least a portion of these groups are etherified with an alcohol to modify the cure response. Any monohydric alcohol may be employed for this purpose including methanol, ethanol, butanol, and hexanol.

Preferably, the aminoplasts which are used are melamine-, urea-, or benzoguanamine-formaldehyde condensates etherified with an alcohol containing from 1 to 6 carbon atoms. The aminoplast is present in amounts of about 1 to 80, preferably 10 to 50 percent by weight based on weight of resin solids in the clear film-forming composition. The equivalent ratio of pendant or terminal carbamate and/or urea functional groups of structure I and II above to methylol or methylol ether groups is 0.5 to 2:1 based on calculated equivalent weights, and being sufficient to form a crosslinked film.

The film-forming composition may be solvent borne, in which the carbamate and/or urea functional materials are dissolved in one or more nonreactive organic solvents. Suitable components of the solvent system which may be used are alcohols such as n-propanol and n-butanol, ethers such as ethylene glycol dibutyl ether and

diethylene glycol dibutyl ether, ketones such as methyl ethyl ketone, methyl isobutyl ketone, methyl amyl ketone and methyl N-butyl ketone; esters such as butyl acetate, 2-ethoxyethyl acetate and hexyl acetate; aliphatic and alicyclic hydrocarbons such as the various
5 petroleum naphthas and cyclohexane; and aromatic hydrocarbons such as toluene and xylene. The amount of solvent used generally can range from about 0 to 55 percent, preferably from about 0 to 50 percent, and most preferably from about 40 to 50 percent by weight based on the total weight of the coating composition.

10 The film-forming composition may also be waterborne. For example, acid-functional materials having terminal or pendant carbamate and/or urea groups may be neutralized with amines and dissolved or dispersed in water. Also, it is possible to prepare an aqueous dispersion of a blend of acrylic and polyester and/or
15 polyurethane materials with pendant carbamate and/or urea groups in microparticulate form by a high stress technique using a homogenizer. This technique is described in U.S. Patent No. 5,071,904.

Powder coatings, i.e., film-forming composition is a solid,
20 may also be prepared from the carbamate and/or urea functional materials of the present invention. Monomers used to form the carbamate and/or urea functional materials are selected such that the resultant material has a high glass transition temperature (T_g); that is, greater than 60°C. This material can then be combined with an
25 aldehyde condensate of glycoluril as mentioned above to form the resinous binder portion of the powder coating composition. Preferably, the film-forming composition is a liquid.

The film-forming composition will also preferably contain catalysts to accelerate the cure of the aminoplast and carbamate or
30 urea groups. Examples of suitable catalysts are acidic materials and include sulfonic acids or substituted sulfonic acids such as para-toluenesulfonic acid. The catalyst is usually present in an amount of about 0.5 to 5.0 percent by weight, preferably about 1 to 2 percent by weight, based on weight of total resin solids. Optional
35 ingredients such as, for example, plasticizers, flow controllers, anti-oxidants, UV light absorbers and similar additives conventional

in the art may be included in the composition. These ingredients are typically present at up to 25% by weight based on total resin solids.

The composition may be applied to a substrate, or in the case of a clear film-forming composition, to a basecoated substrate by any conventional coating technique such as brushing, spraying, dipping or flowing, but spray applications are preferred because of superior gloss. Any of the known spraying techniques may be employed such as compressed air spraying, electrostatic spraying and either manual or automatic methods.

10 After application of the coating composition, the coated substrate is heated to cure the coating. In the curing operation, solvents are driven off and the film-forming material of the coating is crosslinked. The heating or curing operation is usually carried out at a temperature in the range of from 160-350°F (71-177°C) but if 15 needed, lower or higher temperatures may be used as necessary to activate crosslinking mechanisms. The thickness of the coating is usually from about 0.5-5, preferably 1.2-3 mils.

The invention will further be described by reference to the following examples. Unless otherwise indicated, all parts are by 20 weight.

EXAMPLES

The following examples (Examples A-N) show the preparation of carbamate and/or urea functional materials and corresponding 25 hydroxyl functional materials.

Example A

A carbamate functional acrylic monomer was prepared from the following ingredients:

30	<u>Ingredient</u>	<u>Weight in Grams</u>
	isophorone diisocyanate (IPDI)	888.0
	dibutyl tin dilaurate	4.6
	2,6-di-t-butyl methyl phenol	2.6
	butyl methacrylate	282.0
35	hydroxypropyl carbamate	571.2
	hydroxyethyl methacrylate	416.0

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A suitable reactor was charged with the first four ingredients and heated to a temperature of 60°C. The hydroxypropyl carbamate was added to the reaction mixture over 2 hours. The reaction mixture was then held at 60°C until the isocyanate equivalent weight became constant. The hydroxyethyl methacrylate was then added over 2 hours, and the reaction held until infrared analysis indicated the absence of isocyanate. The product was diluted with 346.0 g of butyl methacrylate. The final product had a solids content of 75% and had a number average molecular weight of 622 as determined by gel permeation chromatography.

Example B

A low molecular weight, carbamate functional material was prepared from the following ingredients:

<u>Ingredient</u>	<u>Weight in Grams</u>
DESMODUR N-3300 ¹	3300.0
dibutyl tin dilaurate	4.0
butyl acetate	1592.0
methanol	613.7

¹ Isocyanurate of hexamethylene diisocyanate, available from Miles, Inc.

A suitable reactor was charged with the first three ingredients and heated to a temperature of 60°C. The methanol was added to the reaction mixture over 2 hours. The temperature rose to 74°C and then was held at 80°C until infrared analysis indicated the absence of isocyanate (one and a half hours). The final product had a Gardner-Holdt viscosity of N-0 and a number average molecular weight of 961 as determined by gel permeation chromatography.

Example C

A hydroxyl functional acrylic polymer was prepared from the following ingredients:

	<u>Ingredient</u>	<u>Weight in Grams</u>
	hydroxyethyl acrylate	200.0
	butyl methacrylate	584.0
	α -methyl styrene dimer	16.0
5	LUPERSOL 555M60 ¹	80.0
	t-butyl perbenzoate	24.0

¹ t-amyl peracetate available from Atochem.

A blend of EKTAPRO EEP (ethyl 3-ethoxypropionate available from Eastman Chemicals, 236.8 g) and butyl acetate (105.2 g) was charged to a suitable reactor and heated to reflux. The first three ingredients were mixed with 50 g EKTAPRO EEP. The t-amyl peracetate and 80 g EKTAPRO EEP were also mixed together. The premixture of acrylic monomers and the premixture of initiator were added simultaneously to the reaction vessel over a period of about 3 hours while maintaining the reaction at reflux. At the completion of the addition, the reaction mixture was held at reflux for one hour followed by the addition of 8.0 g t-butyl perbenzoate over about 30 minutes. The reaction was then held for 30 minutes at reflux. 8.0 more grams of t-butyl perbenzoate was added over 30 minutes and the reaction held for 30 minutes at reflux. The remainder of t-butyl perbenzoate was added over 30 minutes and the reaction held at reflux for two hours. An additional total of about 54 grams of EKTAPRO EEP was added to the reaction mixture to adjust the solids content to about 60%. The reaction mixture was then cooled to room temperature. The final product had a solids content of 57% and had a number average molecular weight of 1220 as determined by gel permeation chromatography. The acrylic polymer had a hydroxyl number of about 92.2 based on solids.

30

Example D

A carbamate functional acrylic polymer was prepared from the following ingredients:

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	<u>Ingredient</u>	<u>Weight in Grams</u>
	butyl acetate	332.0
	EKTAPRO EEP	103.0
5	carbamate functional acrylic monomer from Example A	349.9
	butyl methacrylate	279.1
	α -methyl styrene dimer	12.5
	t-amyl peracetate	63.2
	butyl acetate	81.4
10	A suitable reactor was charged with the first two ingredients and heated to reflux. The carbamate functional acrylic monomer, butyl methacrylate and α -methyl styrene dimer were added to the reaction mixture over 3 hours. The t-amyl peracetate and butyl acetate were then added over 3.5 hours. The reaction was then held	
15	at reflux for one hour, and cooled to room temperature. The final product had a solids content of 49.9% and had a number average molecular weight of 1346 as determined by gel permeation chromatography. The carbamate equivalent weight of the resultant material was approximately 900.	

20

Example E

A carbamate functional acrylic polymer dispersed in aqueous medium was prepared from the following ingredients:

	<u>Ingredient</u>	<u>Weight in Grams</u>
25	n-propanol	350.0
	butyl acrylate	202.0
	methyl methacrylate	195.2
	carbamate functional acrylic monomer from example A	349.9
30	acrylic acid	25.0
	t-dodecyl mercaptan	3.2
	t-butyl peroctoate	14.4
	n-propanol	46.4
	dimethyl ethanol amine (DMEA)	23.2
35	water	700.0

A suitable reactor was charged with the n-propanol and heated to reflux. The next five ingredients were added to the reaction mixture over 3 hours. At the same time, the t-butyl peroctoate and 46.4 g n-propanol were added over 3.5 hours. The reaction was then held at reflux for one hour. The DMEA was added to the reaction mixture at about 95°C, followed by addition of the water. The reaction cooled to room temperature. The final product had a solids content of 35.3% and had a number average molecular weight of 3728 as determined by gel permeation chromatography. The carbamate equivalent weight of the resultant material was approximately 1040.

Example F

A carbamate functional acrylic latex was prepared from the following ingredients:

	<u>Ingredient</u>	<u>Weight in Grams</u>
Feed A:	water	783.4
	ALIPAL CO-436 ¹	15.1
	sodium bicarbonate	1.8
20 Feed B:	water	114.8
	ammonium persulfate	5.2
Feed C:	butyl acrylate	277.5
	methyl methacrylate	263.7
25	carbamate functional acrylic monomer from Example A	502.0
	butyl methacrylate	136.9
	acrylic acid	36.4
	t-dodecyl mercaptan	18.2
	water	757.7
30	ALIPAL CO-436	17.4
	DDBSA-DMEA ²	11.5
Feed D:	diisopropanol amine, 50% in water	67.2

¹ Anionic ethoxylated nonyl phenol available from GAF Corporation.

² DDBSA-DMEA solution was prepared by dissolving 1 mole dodecyl benzene sulfonic acid in water containing 1 mole dimethyl ethanolamine.

A suitable reactor was charged with Feed A and heated to 80°C. 25 g of Feed C and then all of Feed B were added to the reaction mixture, and the mixture was held for 20 minutes. The remainder of Feed C was added over 3 hours. The reaction was held at 80°C for two hours, and then cooled to room temperature. After dilution with Feed D, the final product had a solids content of 42.8% and had a number average molecular weight of 12,393 as determined by gel permeation chromatography. The carbamate equivalent weight of the resultant material was approximately 1140.

10

Example G

A urea functional polyester oligomer was prepared from the following ingredients:

	<u>Ingredient</u>	<u>Weight in Grams</u>
15	Methylhexahydrophthalic anhydride	840.95
	hydroxyethylethylene urea ¹	1275.47
	butyl stannic acid	2.12
	triphenyl phosphite	4.23
	xylene	226.1
20	water	101.7
	n-propanol	406.9

¹ Available from Union Carbide as UCar RD-65-1.

The first five ingredients were charged to a suitable reactor equipped with a nitrogen sparge and Dean-Stark trap and heated to reflux. As water was removed from the reaction (88.2 g), the acid value of the reaction mixture dropped to less than 5. The reaction mixture was then vacuum stripped to remove xylene, cooled to 70°C, and diluted with the n-propanol and water. The reaction mixture had a final measured solids content of 77%, a number average molecular weight of 177 and a weight average molecular weight of about 247 as determined by gel permeation chromatography using a polystyrene standard.

30

Example H

A carbamate functional polyester oligomer was prepared from the following ingredients:

35

	<u>Ingredient</u>	<u>Weight in Grams</u>
	Methylhexahydrophthalic anhydride	505.68
	ESTERDIOL 204 ¹	716.04
	butyl stannous acid	2.12
5	urea	120
	xylene	50
	n-propanol	1180
	¹ 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate available from Union Carbide.	

10 The first three ingredients were charged to a suitable reactor equipped with a nitrogen sparge and Dean-Stark trap and heated to reflux. As water was removed from the reaction, the acid value of the reaction mixture dropped to less than 1. The reaction mixture was then cooled to 150°C, and the urea and xylene were
15 added. The reaction mixture was held at reflux for 28 hours and then vacuum stripped to remove xylene. After dilution with the n-propanol, the reaction mixture had a final measured solids content of 52.6%, and a viscosity of A on the Gardner-Holdt scale.

20

Example I

A carbamate functional polyester was prepared from the following ingredients:

	<u>Ingredient</u>	<u>Weight in Grams</u>
	DOWANOL PM carbamate ²	332.5
25	polyester ¹	455
	butyl stannous acid	2.12

¹ Reaction product of hexahydrophthalic anhydride, ESTERDIOL 204, and 1,6-hexanediol in a 1:1:1 mole ratio.

² Reaction product of DOWANOL PM and urea, 95% in DOWANOL PM
30 which is the monomethyl ether of propylene glycol and is available from Dow Chemical Co.

The ingredients were charged to a suitable reactor equipped with a nitrogen sparge and Dean-Stark trap and heated to 140-145°C. DOWANOL PM was removed from the reaction under reduced pressure. The
35 reaction mixture was held until DOWANOL PM carbamate was no longer detectable on a gas chromatograph. The resultant reaction mixture was a soft, waxy, opaque material.

Example J

A pre-emulsion was prepared by stirring together the following ingredients:

	<u>Ingredient</u>	<u>Weight in Grams</u>
5	carbamate functional polyester of Example I	125.0
	methyl methacrylate	100.0
	butyl acrylate	100.0
	stearyl methacrylate	25.0
10	N-methylol acrylamide (48% solution in water)	83.4
	methacrylic acid	10.0
	dodecylbenzenesulfonic acid (70% in water)	14.3
	N,N-dimethyl ethanol amine	2.5
15	IGEPAL CO-897 ¹	7.2
	ferrous ammonium sulfate, 1% in water	2.5
	water	500.0

¹ Nonionic ethoxylated nonyl phenol available from GAF Corp.

The pre-emulsion was passed through an M110 MICROFLUIDIZER high pressure impingement emulsifier (available from Microfluidics, Inc.) at 8000 psi to produce a bluish-white emulsion. The emulsion was transferred to a suitable reactor and blanketed with nitrogen. Polymerization was initiated by adding first a mixture of 1.5 g isoascorbic acid and 2.5 g mercaptopropionic acid dissolved in 50.0 g water followed by a solution of 2.19 g hydrogen peroxide (35%) in 25.0 g water added dropwise over 15 minutes. The emulsion exothermed from 26 to 66°C over 14 minutes. Any remaining monomer was then polymerized by adding 0.5 g isoascorbic acid dissolved in 5.0 g water followed by 0.5 g of 35% hydrogen peroxide. An additional exotherm from 56 to 59°C was observed. The pH of the latex was increased to 7.0 with 16.45 g of a 1:1 mixture of water and diisopropanolamine. The final product had a solids content of 41.0%.

Example K

A urea functional polyester oligomer was prepared from the following ingredients:

	<u>Ingredient</u>	<u>Weight in Grams</u>
	dodecanedioic acid	575.0
	hydroxyethyl ethylene urea	637.74
	butyl stannic acid	1.21
5	xylene	198.66

The ingredients were charged to a suitable reactor and heated to reflux to remove water through a Dean-Stark trap. The temperature of the reaction mixture was held at reflux until the acid value was less than 5. The reaction mixture was then cooled to 120°C and volatile materials in the reaction mixture were removed under vacuum to a solids content of 98.7%. The reaction mixture was diluted to a final solids content of 65% with an 80:20 weight mixture of propanol:water. The product had a number average molecular weight of 606 and a urea equivalent weight of approximately 230.

15

Example I

A carbamate functional acrylic monomer was prepared from the following ingredients:

	<u>Ingredient</u>	<u>Weight in Grams</u>
20	hydroxypropyl carbamate	600.0
	2,6-di-t-butyl methyl phenol	3.9
	triphenyl phosphite	2.22
	methacrylic anhydride	810.0
	toluene	1200.0
25	sodium hydroxide (16.7%)	1260.0

A suitable reactor was charged with the first four ingredients and heated to 100°C. The reaction mixture was held at this temperature until the methacrylic anhydride had completely reacted with the hydroxypropyl carbamate, as determined by gas chromatography. The reaction was cooled to room temperature and the toluene and sodium hydroxide were added. After agitating for about 30 minutes, the reaction mixture was transferred to a separatory funnel. The top layer, containing the product in toluene, was collected in a flask and the toluene was removed by vacuum distillation.

35

Example M

A carbamate functional acrylic latex was prepared from the following ingredients:

	<u>Ingredient</u>	<u>Weight in Grams</u>
5	Feed A: water	450.0
	ALIPAL CO-436	9.3
	sodium bicarbonate	0.8
	Feed B: water	50.0
	ammonium persulfate	2.2
10	Feed C: carbamate functional acrylic monomer of Example L	180.0
	butyl acrylate	240.0
	methyl methacrylate	120.0
	styrene	60.0
15	acrylic acid	16.8
	t-dodecyl mercaptan	9.0
	water	400.0
	ALIPAL CO-436	18.0
	PGNP-15 ¹	26.0
20	Feed D: diisopropanol amine, 50% in water	20.0

¹ Nonionic surfactant prepared by reacting 1 mole of nonyl phenol with 15 moles of glycidol.

A suitable reactor was charged with Feed A and heated to 80°C. 25 g of Feed C and then all of Feed B were added to the reaction mixture, and the mixture was held for 20 minutes. The remainder of Feed C was added over 3 hours. The reaction was held at 80°C for two hours, and then cooled to room temperature. After addition of Feed D, the pH was 7.7. The final product had a solids content of 40.5% and had a number average molecular weight of 5706 as determined by gel permeation chromatography.

Example N

A hydroxyl functional acrylic latex was prepared from the following ingredients:

	<u>Ingredient</u>	<u>Weight in Grams</u>
	Feed A: water	450.0
	ALIPAL CO-436	9.3
	sodium bicarbonate	0.8
5	Feed B: water	50.0
	ammonium persulfate	2.2
	Feed C: hydroxyethyl acrylate	180.0
	butyl acrylate	240.0
	methyl methacrylate	120.0
10	styrene	60.0
	acrylic acid	16.8
	t-dodecyl mercaptan	9.0
	water	400.0
	ALIPAL CO-436	18.0
15	PGNP-15	26.0
	Feed D: diisopropanol amine, 50% in water	20.0

A suitable reactor was charged with Feed A and heated to 80°C. 25 g of Feed C and then all of Feed B were added to the reaction mixture, and the mixture was held for 20 minutes. The remainder of Feed C was added over 3 hours. The reaction was held at 80°C for two hours, and then cooled to room temperature. After addition of Feed D, the pH was 7.84. The final product had a solids content of 40.2% and had a number average molecular weight of 5123 as determined by gel permeation chromatography, and a hydroxyl value of 22 based on solids content.

The following examples (1-12) show the preparation of various clear film-forming compositions prepared with carbamate, urea, or hydroxyl functional materials and aminoplast curing agents. The coating compositions were evaluated in color-plus-clear applications.

Example 1

A clear film-forming composition was prepared by mixing together the following ingredients:

	<u>Ingredient</u>	<u>Solid weight in grams</u>	<u>Solution weight in grams</u>
	n-butyl acetate	---	7.0
	EKTAPRO EEP	---	19.0
	TINUVIN 1130 ¹	3.0	3.0
5	TINUVIN 292 ²	0.3	0.3
	polybutylacrylate ³	0.4	0.7
	flow control agent ⁴	1.0	2.3
	CYMEL 327 ⁵	30.0	33.3
	carbamate containing		
10	acrylic of Example D	69.0	138.8
	phenyl acid phosphate	1.0	1.2

¹ Substituted benzotriazole UV light stabilizer available from Ciba Geigy Corporation.

² Sterically hindered tertiary amine light stabilizer available from Ciba Geigy Corporation.

³ A flow control agent having a Mw of about 6700 and Mn of about 2600 made in xylene at 62.5% solids.

⁴ Polymeric microparticle prepared in accordance with example 11 of U.S. Patent No. 4,147,688.

⁵ Highly methylated, high imino content aminoplast resin available from American Cyanamid.

Example 2

A clear film-forming composition was prepared by mixing together the following ingredients:

	<u>Ingredient</u>	<u>Solid weight in grams</u>	<u>Solution weight in grams</u>
	hexyl acetate	---	7.0
	EKTAPRO EEP	---	15.1
	TINUVIN 1130	3.0	3.0
30	TINUVIN 292	0.3	0.3
	polybutylacrylate	0.4	0.7
	flow control agent	1.0	2.3
	CYMEL 327	30.0	33.3
	carbamate containing		
35	acrylic of Example D	49.0	97.0
	hydroxyl containing		
	acrylic of Example C	20.0	35.1
40	phenyl acid phosphate	1.0	1.2

Example 3

A clear film-forming composition was prepared by mixing together the following ingredients:

<u>Ingredient</u>	<u>Solid weight in grams</u>	<u>Solution weight in grams</u>
5 hexyl acetate	---	7.0
EKTAPRO EEP	---	18.8
TINUVIN 1130	3.0	3.0
TINUVIN 292	0.3	0.3
polybutylacrylate	0.4	0.7
10 flow control agent	1.0	2.3
CYMEL 327	30.0	33.3
carbamate containing acrylic of Example D	29.0	57.3
15 hydroxyl containing acrylic of Example C	40.0	70.1
phenyl acid phosphate	1.0	1.2

20

Example 4

A clear film-forming composition was prepared by mixing together the following ingredients:

<u>Ingredient</u>	<u>Solid weight in grams</u>	<u>Solution weight in grams</u>
hexyl acetate	---	7.0
25 EKTAPRO EEP	---	19.3
TINUVIN 1130	3.0	3.0
TINUVIN 292	0.3	0.3
polybutylacrylate	0.4	0.7
flow control agent	1.0	2.3
30 CYMEL 327	30.0	33.3
carbamate containing acrylic of Example D	9.0	17.8
hydroxyl containing 35 acrylic of Example C	60.0	105.1
phenyl acid phosphate	1.0	1.2

Example 5

40

A clear film-forming composition was prepared by mixing together the following ingredients:

<u>Ingredient</u>	<u>Solid weight in grams</u>	<u>Solution weight in grams</u>
n-butyl acetate	---	7.0
EKTAPRO EEP	---	15.0
TINUVIN 1130	3.0	3.0
5 TINUVIN 292	0.3	0.3
polybutylacrylate	0.4	0.7
flow control agent	1.0	2.3
CYMEL 327	30.0	33.3
hydroxyl containing		
10 acrylic of Example C	69.0	120.7
phenyl acid phosphate	1.0	1.2

Example 6

A clear film-forming composition was prepared by mixing
15 together the following ingredients:

<u>Ingredient</u>	<u>Solid weight in grams</u>	<u>Solution weight in grams</u>
n-amyl alcohol	---	35.1
TINUVIN 1130	3.0	3.0
TINUVIN 292	0.3	0.3
20 polybutylacrylate	0.4	0.7
low molecular weight carbamate functional material of Example B	11.1	15.9
25 carbamate functional acrylic of Example D	32.5	64.2
urea functional polyester of Example G	11.1	14.4
30 carbamate functional polyester of Example H	10.3	17.3
phenyl acid phosphate	1.0	1.2

35 The film-forming compositions of Examples 1-6 were applied
to a pigmented basecoat to form color-plus-clear composite coatings
over electrocoated steel substrates. The pigmented basecoat for
Examples 1-6 is commercially available from PPG Industries, Inc. and
identified as NHU-9517. The basecoat was pigmented black in color.
40 The electrocoat used on the steel is commercially available from PPG
Industries, Inc. and is identified as ED-11.

The basecoat was spray applied in two coats to electrocoated steel panels at a temperature of about 75°F (24°C). A ninety second flash time was allowed between the two basecoat applications. After the second basecoat application, a flash time of approximately five minutes was allowed at 75°F (24°C) before the application of the clear coating composition. The clear coating compositions of Examples 1-6 were each applied to a basecoated panel in two coats with a ninety second flash at 75°F (24°C) allowed between coats. The composite coating was allowed to air flash at 75°F (24°C) for ten to fifteen minutes before baking at 285°F (141°C) for 30 minutes to cure both the basecoat and clearcoat. The panels were baked in a horizontal position. The properties of the composite coatings are reported in Table I below.

Table I

Example	Hydroxyl Number of Composition	% OH Functional Resin by Weight	Acid Etch Rating*	Pencil Hardness After 3 Minute Xylene Spot**
1	0	0	3	F
2	23	20	4	F
3	46	40	5	F
4	69	60	8	F
5	115	100	8	H
6	0	0	3	H

*Panels were sprayed with a sulfurous acid solution (350 grams deionized water and 12 grams sulfurous acid to give a pH of 2.0 plus or minus 0.1) using a polyethylene spray bottle, giving a distribution of drop sizes up to one quarter inch. Approximately 2.5 to 3.0 grams of solution were applied per 4x4 inch panel. The panels were then placed in an oven at 110°F (43°C) for twenty minutes. The panels were removed from the oven and the spray/bake procedure was repeated two more times to give a total of 60 minutes at 110°F (43°C). After the third cycle the panels were washed with soap and water and dried, then rated for degree of acid etch resistance on a scale of 1-10 (1 = no observable etching; 10 = severe etching).

**Pencil hardness (Gouge hardness) determined by ASTM D 3353-74 was performed immediately after the panel was spotted with a 0.5 inch to 2 inch drop of xylene and wiped dry.

Example 7

A clear film-forming composition was prepared by mixing together the following ingredients:

<u>Ingredient</u>	<u>Solid weight in grams</u>	<u>Solution weight in grams</u>
5 TINUVIN 1130	3.5	3.5
CYMEL 328 ¹	30.0	34.9
carbamate containing acrylic of Example E	70.0	198.4
phenyl acid phosphate	1.0	5.0
10 water	---	137.0

¹ Waterborne version of CYMEL 327 available from American Cyanamid.

Example 8

15 A clear film-forming composition was prepared by mixing together the following ingredients:

<u>Ingredient</u>	<u>Solid weight in grams</u>	<u>Solution weight in grams</u>
carbamate containing acrylic of Example F	70.0	162.6
20 CYMEL 303 ¹	30.0	30.0
TINUVIN 1130	3.5	3.5
DDBSA solution ²	1.0	5.0
FC 430 solution ³	0.1	2.0
diisopropanol amine solution ⁴	---	3.9
25 n-methyl-2-pyrrolidone	---	5.0
isopropanol	---	5.0
water	---	25.0

¹ Hexamethoxymethyl melamine resin available from American Cyanamid.

30 ² 20 weight percent solution of dodecylbenzene sulfonic acid neutralized with diisopropanolamine in deionized water.

³ Nonionic surfactant available from 3M Corporation.

⁴ 50 weight percent solution of diisopropanolamine in deionized water.

Example 9

A clear film-forming composition was prepared by mixing together the following ingredients:

<u>Ingredient</u>	<u>Solid weight in grams</u>	<u>Solution weight in grams</u>
5 DDDA/HEEU oligomer of Example K	70.0	116.7
CYMEL 328	30.0	34.9
10 Phenyl acid phosphate solution	1.0	5.0
Tego Wet ZFS 453 ¹	0.09	0.36
¹ Nonionic surfactant available from Tego Chemie Service GmbH.		

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Example 10

A clear film-forming composition was prepared by mixing together the following ingredients:

<u>Ingredient</u>	<u>Solid weight in grams</u>	<u>Solution weight in grams</u>
20 carbamate functional acrylic and polyester latex of Example J	70.0	170.61
CYMEL 303	30.0	30.0
TINUVIN 1130	3.5	3.5
25 DDBSA solution	1.0	5.0
FC 430 solution	0.1	2.0
diisopropanol amine solution	—	3.2
n-methyl-2-pyrrolidone	—	5.0
isopropanol	—	5.0
30 water	—	58.1

Example 11

A clear film-forming composition was prepared by mixing together the following ingredients:

	<u>Ingredient</u>	<u>Solid weight in grams</u>	<u>Solution weight in grams</u>
	carbamate functional acrylic latex of Example M	70.0	172.8
	CYMEL 303	30.0	30.0
5	TINUVIN 1130	3.5	3.5
	p-TSA solution ¹	1.0	5.0
	diisopropanol amine solution	—	3.5
	isopropanol	—	50.0
	water	—	17.3
10	¹ 20 weight percent solution of para-toluene sulfonic acid neutralized with diisopropanol amine in water.		

Example 12

A clear film-forming composition was prepared by mixing together the following ingredients:

	<u>Ingredient</u>	<u>Solid weight in grams</u>	<u>Solution weight in grams</u>
	hydroxyl functional acrylic latex of Example N	70.0	174.2
	CYMEL 303	30.0	30.0
20	TINUVIN 1130	3.5	3.5
	p-TSA solution	1.0	5.0
	diisopropanol amine solution	—	3.5
	isopropanol	—	50.0
	water	—	16.3

The film-forming compositions of Examples 7-12 were applied to a pigmented basecoat to form color-plus-clear composite coatings over electrocoated steel substrates. The pigmented basecoat for Examples 7-12 is commercially available from PPG Industries, Inc. and identified as BWB-8555. The basecoat was pigmented black in color. The electrocoat used on the steel is commercially available from PPG Industries, Inc. and is identified as ED-11.

The basecoat was spray applied in two coats to electrocoated steel panels at a temperature of about 75°F (24°C) and a relative humidity of about 60%. A ninety second flash time was allowed between the two basecoat applications. After the second basecoat application, a prebake time of approximately five minutes was allowed

at 250°F (121°C) before the application of the clear coating composition. The clear coating compositions of Examples 7-12 were each applied to a basecoated panel in two coats with a ninety second flash at 75°F (24°C) allowed between coats. The composite coating 5 was allowed to air flash at 75°F (24°C) for ten to fifteen minutes and to flash at 140°F (60°C) for ten to fifteen minutes before baking at 285°F (141°C) for 30 minutes to cure both the basecoat and clearcoat. The panels were baked in a horizontal position. The properties of the composite coatings are reported in Table II below.

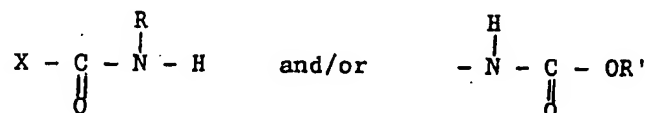
10

Table II

<u>Example</u>		<u>Acid Etch Rating</u>
15	7	3
	8	3
	9	2
	10	5
	11	5
	12	9

We claim:

1. A curable film-forming composition comprising (1) a material containing a plurality of terminal or pendant groups of the structure:



where X is -N or -O and R is H or alkyl of 1-18 carbon atoms or R is bonded to X and forms part of a 5 or 6 membered ring and R' is alkyl of 1 to 18 carbon atoms; and (2) an aminoplast crosslinking agent containing methylol and/or methylol ether groups; said film-forming composition being crosslinkable through reaction of said pendant or terminal groups with said methylol and/or methylol ether groups; said film-forming composition being further characterized as having a calculated hydroxyl value less than 50 based on solid weight of said film-forming composition, excluding any hydroxyl functionality associated with N-methylol groups so as to result in a crosslinked coating which has a substantial number of urethane and/or urea crosslinks arising from said reaction of pendant or terminal groups with said methylol and/or methylol ether groups, giving said crosslinked coating a high level of acid etch resistance.

2. The composition of claim 1 in which the material is an acrylic polymer.

3. The composition of claim 2 in which the acrylic polymer has an equivalent weight less than 5000 based on equivalents of said terminal or pendant groups.

4. The composition of claim 3 in which the acrylic polymer has an equivalent weight within the range of about 140 to 2500 based on equivalents of said terminal or pendant groups.

5. The composition of claim 1 in which the material is selected from the class consisting of polyesters, polyurethanes, and mixtures thereof.

6. The composition of claim 5 in which the material has on average at least two of said terminal or pendant groups per molecule.

7. The composition of claim 6 in which the material has an equivalent weight of from about 140 to 2500 based on equivalents of said terminal or pendant groups.

8. The composition of claim 1 in which X is -O and R is selected from the class consisting of H and alkyl containing from 1 to 6 carbon atoms and R' is alkyl containing from 1 to 6 carbon atoms.

9. The composition of claim 1 in which the aminoplast is a condensate of melamine with formaldehyde and optionally an alcohol containing from 1 to 6 carbon atoms.

15

10. The composition of claim 1 wherein the equivalent ratio of said pendant or terminal groups to methylol or methylol ether groups is from 0.5 to 2:1 and is sufficient to form a crosslinked film.

20

11. The composition of claim 1 wherein the material is present in the film-forming composition in amounts of 50 to 90 percent by weight based on weight of resin solids in the film-forming composition.

25

12. The composition of claim 1 wherein the aminoplast is present in the film-forming composition in amounts of 10 to 50 percent based on weight of resin solids in the film-forming composition.

INTERNATIONAL SEARCH REPORT

Inter. Application No
PCT/US 93/10172

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08F8/30 C09D201/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C08F C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,87 00851 (UCC) 12 February 1987 see page 11 see page 15; claims 1-56 ---	1-12
A	US,A,3 984 382 (G. G. PAREKH) 5 October 1976 see column 7, line 41 - column 8, line 32; claims 1-10 ---	1
A	US,A,3 959 201 (PPG INDUSTRIES, INC.) 25 May 1976 see claims 1-19 ---	1
A	WO,A,91 08269 (BOLLIG & KEMPER KG) 13 June 1991 see claims 1-17 ---	1
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

30 March 1994

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/10172

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 374 340 (BASF CORPORATION) 27 June 1990 see page 3, line 44 - page 4, line 27; claims 1-8 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter Application No

PCT/US 93/10172

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-8700851	12-02-87	CA-A- 1295767 EP-A- 0233253 JP-B- 1049747 JP-T- 63501576	11-02-92 26-08-87 25-10-89 16-06-88
US-A-3984382	05-10-76	NONE	
US-A-3959201	25-05-76	US-A- 3994851 CA-A- 1028079 DE-A- 2447812 FR-A, B 2247518 GB-A- 1491014 JP-C- 931912 JP-A- 50066529 JP-B- 52000971	30-11-76 14-03-78 17-04-75 09-05-75 09-11-77 07-11-78 04-06-75 11-01-77
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EP-A-0374340	27-06-90	US-A- 4837278	06-06-89

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